```
ANSWER 1  CA  COPYRIGHT 1999 ACS
AN    107:221999  CA
TI    Method of manufacture of transparent heat-reflecting doped tin dioxide on
      glass
IN    Kavka, Jan
PA    Czech.
SO    Czech., 3 pp.
      CODEN: CZXXA9
DT    Patent
LA    Czech
IC    ICM  C03C017-23
CC    57-1 (Ceramics)
FAN.CNT 1
      PATENT NO.         KIND  DATE            APPLICATION NO.   DATE
      ---------------    ----  --------        ---------------   --------
PI    CS 239788          B1    19860116        CS 1984-5724      19840725
AB    Layers of Sb- or F-doped SnO2 that reflect 60-75% radiation in the region
      of 5-12 .mu. and transmit 63-85% of visible light are formed on the
      surface of glass preheated to 350-750.degree. by contact with decompg.
      org. or inorg. Sn compd. contg. a decompg. Sb or F additive.  The concn.
      of Sb or F as an electroactive additive is 5-10% depending on the glass
      temp.  The low deposition temp. allows modification of sheet glass leaving
      the forming process and saves energy in coating of glass tubes and lamp
      bulbs.  A borosilicate glass tube was heated to 570.degree. and sprayed
      with a soln. contg. 100 g Me2SnCl2, 100 H2O, and 9.4 mL HF to prep. a
      homogeneous SnO2 layer contg. 6% F reflecting 65-75% radiation of
      wavelength 5-12 .mu. and transmitting 75-85% of the visible light.
ST    reflecting fluorine doped tin oxide layer; glass oxide coating reflecting
      layer; antimony dopant tin oxide glass; dopant fluorine tin oxide glass
IT    Optical reflection
         (IR, by antimony- or fluorine-doped tin oxide on glass)
IT    Optical reflectors
         (IR, glass, with antimony- or fluorine-doped tin oxide layers)
IT    18282-10-5, Tin dioxide
      RL: USES (Uses)
         (antimony- or fluorine-doped, coatings, on glass, for IR-radiation
         reflection)
IT    753-73-1, Dimethyltin dichloride   7664-39-3, Hydrogen fluoride, reactions
      RL: RCT (Reactant)
         (decompn. of, in coating of glass with doped tin oxide for IR-radiation
         reflection)
IT    7440-36-0, Antimony, uses and miscellaneous   7782-41-4, Fluorine, uses
      and miscellaneous
      RL: USES (Uses)
         (dopant, tin oxide layer contg., on glass for IR-radiation reflection)
```

A M

Method of manufacture of transparent heat-reflecting doped tin dioxide on glass

Auteur(s)/Inventeur(s) : Kavka J

Déposants : Czech. (CS)

Données de Publications :
N° Dépôt : CS1984/5724 19840725 [1984CS-0005724]
Source de Document :
Type Document : Patent
Langue : Cze
Numéro d'accés : 107-221999
Numéro Volume : 107-24
Section Principale : S57-001/1982

Descripteurs :
Mots-Clés : 753-73-1 (C2H6Cl2Sn); 7664-39-3 (FH), reactions: (decompn. of, in coating of glass with doped tin oxide for IR-radiation reflection)
7440-36-0 (Sb), uses and miscellaneous; 7782-41-4 (F2), uses and miscellaneous: (dopant, tin oxide layer contg., on glass for IR-radiation reflection)
18282-10-5 (O2Sn): (antimony- or fluorine-doped, coatings, on glass, for IR-radiation reflection)
-Optical reflection-, IR: (by antimony- or fluorine-doped tin oxide on glass)
-Optical reflectors-, IR: (glass, with antimony- or fluorine-doped tin oxide layers)
Mots-Clés compl. : reflecting fluorine doped tin oxide layer; glass oxide coating reflecting layer; antimony dopant tin oxide glass; dopant fluorine tin oxide glass

FURTHER TRANSLATION
TRANSLATION FROM CZECH of Ref. AM of record; IDS dated 02/14/00

(19) Czechoslovak Socialist Republic Bureau for Inventions and Discoveries
(11) Czechoslovak Patent 220,175 (B1)
(51) Int. Cl.[3] C 03 C 17/23
(22) Filed: 04.12.81
(21) (PV 9007-81)
(40) Laid open: 27.08.82
(45) Issued: 15.10.85
(75) Inventor: J. Kavka, HRADEC KRÁLOVÉ

(54) Process for producing transparent heat-reflective layers of tin dioxide on glass

The invention solves the problem of achieving maximum infrared reflectivity of thin transparent heat-reflective layers on glass.

The surface of heated glass is brought into contact with a medium containing at least one decomposable organic or inorganic compound of tin and at least one decomposable compound of an electrically active mixture derived from a group comprising fluorine and antimony, for a period which is sufficient for the formation of a tin dioxide layer, the precise concentration of the mixture being chosen such as to be in the range from 0.5 to 5% by weight depending on the temperature of the heated glass.

EXHIBIT A

The invention relates to a process for producing transparent heat-reflective layers of tin dioxide, on a glass substrate.

One possibility of reducing the energy consumption for the heating of buildings in winter is to reduce heat losses from the inside through windows to the outer environment by means of heat-reflective, transparent thin layers on glass. These layers reflect long-wave heat radiation back to the inside, thereby enhancing the heat-insulating properties of the windows. A highly advantageous and in recent times an intensively developed type of heat-reflective layers are semiconducting layers based on tin Sn or indium In oxides, doped for the purpose of increasing reflectivity with suitable electrically active mixtures, most often with fluorine F or antimony Sb.

A number of processes exist for applying these layers. One of the most advantageous and most frequently used methods is the thermal decomposition of a suitable compound which is brought into contact with the surface of the heated glass either in the liquid (aerosol spray, dipping and extraction from solution, glazing etc.) or gaseous (applying a mixture of gases to the surface) phase. The principle of this method has been known for a long time; according to US patent 2,564,708 a whole range of heat-reflective oxide layers can be formed by hydrolysis of metal salts. A further enhancement of this process including improved design of the necessary equipment is disclosed, for example, in East German patent 2,716,183, French patent 2,348,167, British patent 1,506,668, Australian patent 482,853 and USSR patent 269,226.

The most important characteristic of the heat-reflective layers is the attainment of the highest possible value in infrared reflectivity without any reduction of transmission in the visible part of the spectrum. The processes known hitherto solved the problem of maximum reflectivity in the infrared region by the choice of a suitable concentration of electrically active mixtures determined experimentally. It is known that the content of fluorine F or antimony Sb must be kept within certain boundaries, a lower or higher concentration producing a reduction of either reflectivity or transmission in the visible part of the spectrum.

However, it has now been established by numerous experiments that the optimum concentration of electrically active mixtures is not a constant but one which depends on application temperature. At different application temperatures, maximum infrared reflectivity and transmission in the visible part of the spectrum are different for different concentrations of the mixtures. If the fluorine F or antimony Sb contents are determined without regard to the application temperature, as would be the case with hitherto known methods, the attainment of maximum infrared reflectivity and transmission in the visible part of the spectrum cannot be assured in all cases.

The above drawbacks are overcome by the process of producing transparent heat-reflective layers of tin dioxide SnO_2 according to the invention, which consists in bringing the surface of heated glass into contact with a medium containing at least one

decomposable organic or inorganic compound of tin Sn and at least one decomposable compound of an electrically active mixture derived from a group comprising fluorine F or antimony Sb, for a period which is sufficient for the formation of a tin dioxide SnO_2 layer, the precise concentration of the mixture being chosen such as to be in the range from 0.5 to 5% by weight depending on the temperature of the heated glass. The temperature at which the layers are applied, cannot be precisely specified in advance; it is governed in addition to the types of initial compounds used, by the application technique, the composition of the glass substrate, its viscosity and other parameters. From the combination of these influences there results a given value for the temperature which the glass should attain while the layers are applied. It is only on the basis of this temperature that the precise concentration of the mixture - fluorine F or antimony Sb - is experimentally determined (by measuring the reflectivity of a series of samples each with a variable content of the electrically active mixture) with the aim of achieving the highest possible infrared reflectivity.

Glass coated with a heat-reflective layer according to the invention is suitable for use in heat-insulating glazing of buildings with the aim of reducing heat losses from the inside to the outer environment in winter. Energy saving can in the case of double-glazed windows coated with reflective layers be as high as 50%.

A few examples of producing heat-reflective layers on float glass will best elucidate the invention.

Example 1

Float glass, 3 mm thick, is heated to 640°C and the surface is then sprayed, over a period of 10 seconds using a spray gun, with the solution produced by mixing 100 g of tin dimethyl dichloride $(CH_3)_2SnCl_2$, 100 ml of distilled water H_2O and 3.9 ml of hydrofluoric acid HF. A homogeneous layer of tin dioxide SnO_2 containing 2.5% by weight of fluorine F forms on the glass; it has a uniform light green colour in reflection, a transmission in the visible part of the spectrum of 70-87% and a reflectivity in the region from 5 to 12 μm in the range of 70-80%.

Example 2

Float glass, 3 mm thick, is heated to 650°C and the surface is then sprayed, over a period of 8 seconds using a spray gun, with a solution produced by mixing 100 g of tin dimethyl dichloride $(CH_3)_2SnCl_2$, 100 ml of distilled water H_2O and 5.2 ml of hydrofluoric acid HF. A homogeneous layer of tin dioxide SnO_2 containing 3.5% by weight of fluorine F forms on the glass; it has a uniform light green colour in reflection, a transmission in the visible part of the spectrum of 70-85% and a reflectivity in the region from 5 to 12 μm in the range of 70-80%.

Example 3

Float glass, 5 mm thick, is heated to 580°C and the surface is then treated, over a period of 6 seconds, with a gaseous mixture produced by mixing vapours from stannic chloride $SnCl_4$ and antimony trichloride $SbCl_3$ in the ratio 1:0.8. A homogeneous layer of tin dioxide SnO_2 containing approx. 1% of antimony Sb forms on the glass; it has a uniform light green colour in reflection, a transmission in the visible part of the spectrum of 70-80% and a reflectivity in the region from 5 to 12 μm in the range of 65-75%.

CLAIM

A process for producing transparent heat-reflective layers of tin dioxide on glass, consisting in bringing the surface of heated glass into contact with a medium containing at least one decomposable organic or inorganic compound of tin and at least one decomposable compound of an electrically active mixture derived from a group comprising fluorine and antimony for a period which is sufficient for the formation of a tin dioxide layer, characterized in that the concentration of the electrically active mixture is chosen such as to be in the range from 0.5 to 5% by weight depending on the concrete temperature of the heated glass.